CATALYTIC REDUCTION OF SULFUR DIOXIDE TO ELEMENTAL SULFUR

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Keywords: sulfur dioxide, catalytic conversion, elemental sulfur

INTRODUCTION

There are several regenerable flue gas desulfurization processes; some of them have been commercilized, while others are still emerging. In the regenerable processes, sulfur dioxide from flue gas is first absorbed into an alkaline solution (Wellman-Lord, Tung, Cansolv, and Dow processes) or adsorbed on a solid substrate (NOXSO and CuO processes), and is subsequently desorbed to produce a stream of high concentration sulfur dioxide. It is desirable to convert sulfur dioxide to elemental sulfur for storage, transportation, and/or conversion to valuable chemicals.

Sulfur dioxide can be reduced with synthesis gas, derived from coal ($H_2/CO = 0.3-1.0$) or methane ($H_2/CO = 3$), to produce elemental sulfur at elevated temperatures according to the reaction

$$0.875 \text{ SO}_2 + 0.75 \text{ H}_2 + \text{CO} \longrightarrow 0.438 \text{ S}_2 + \text{CO}_2 + 0.75 \text{ H}_2\text{O}$$
 (1)

$$2 SO_2 + 3 H_2 + CO \longrightarrow S_2 + CO_2 + 3 H_2O$$
 (2)

These reactions are facilitated with catalysts. In addition to elemental sulfur, these reactions may produce several undesirable byproducts. These include hydrogen sulfide, carbonyl sulfur dioxide and high selectivity to elemental sulfur at low temperatures. However, the results obtained so far show only limited successes and do not warrant a commercial application. Using synthesis gas to reduce SO2, Akhmedov et. al. [1] developed several catalysts and obtained the following results: a 64-65 % sulfur yield with a bauxite-bentonite catalysts at 350 C with a feed gas at a molar ratio (CO + H2)/SO2 of 2 and a space velocity of 1000 h⁻¹; a 82.0 % sulfur yield with a NiO/Al2O3 catalyst at 300 C with a space velocity of 500 h⁻¹ [2]; a 82.0 % and 87.4 % sulfur yield with a Co2O3/Al2O3 catalyst [3] at 300 C with a space velocity of 1000 h⁻¹ and 500 h⁻¹ respectively; a 82.3 % and 78.6 % sulfur yield with a NiO-Co3O4 catalyst [4] at 400 C with a space velocity of 500 h⁻¹ and 1000 h⁻¹ respectively. The development of a catalyst capable of obtaining better than 90 % yield of sulfur with a high space velocity at low temperatures would be required to warrant a commercial application. This paper reports the evaluation results of a promising catalyst formulated in our lab.

EXPERIMENTAL

Catalyst Preparation

Catalysts were composed of a combination of several metal oxides supported on -Al₂O₃. Two sizes of -Al₂O₃ were used: 1. 30-40 mesh particles, and 2. 3mm dia. by 5 mm height granules. By mixing appropriate amounts of metal nitrate solutions with -Al₂O₃, the mixture underwent stepwise heating to form the activated catalyst. The ratio of the active catalyst to carrier was about 0.3 by weight.

Apparatus and Procedure

A schematic flow diagram of the apparatus is shown in Figure 1. The experimental setup consists of three separate sections: the gas supply section, the main reactor, and the detection and analysis section. Gases are supplied from compressed gas cylinders (Matheson Gas Products) to gas flow meters before entering a gas mixer. The tubular reactor is fabricated from a 1.4-cm-o.d. with a 1-mm wall thickness quartz tube. The entire reactor is mounted inside a tubular furnace. The reactor, which is 5 cm long, consists of three zones. The inlet or the preheating zone (2.5 cm long) is packed with 20 mesh quartz chips, the reaction zone (1.5 cm long) is packed with either particles (30-40 mesh) or granules (d. 3mm x h. 5mm) activated catalysts on alumina, and the outlet zone (1 cm long) is packed with quartz chips (20 mesh), mainly for the purpose of supporting the catalyst, which sat on a perforated quartz plate having seven holes for gas exit. A thermocouple, reaching the center of the catalytic packing, provide measurement of the temperature of catalytic reactions. After the last section of the reactor, the gases pass through a sulfur collector at room temperatures, and then enter into an on-line trap cooled in an ice bath to condense water before entering a six-port sampling valve which is used to inject the products of the catalytic reactions into the gas chromatograph. Finally, the exit gases pass into a scrubber containing concentrated NaOH.

The inlet and exit gases are analyzed by using a gas chromatograph equipped with a column switching valve and a thermal conductivity detector. A 2-meter Porapak QS (80-100 mesh) column was employed. The operating conditions were at 60 mA and at column temperature of 100 C. The carrier gas is helium.

RESULTS AND DISCUSSION

The inventive catalyst (Cat-S) consists of active metal oxide components and carriers (-Al₂O₃). In order to study the kinetics of the reactions and the diffusivity of the reactants, two carrier sizes were used. The smaller size carrier is 30-40 mesh -Al₂O₃ particles, which were used typically in laboratory scale experiments to obtain kinetic information. The larger size carrier has a dimension of 3 mm diameter by 5 mm height cylindrical granules, which were used in scale up tests. The parametric studies were conducted on particles and granules for comparison. The lifetime experiments were performed on particles.

Particles (30-40 mesh)

Parametric Studies

The effect of temperatures, space velocity, molar ratios of reductants to $SO_2(R = F_{H2+CO)}/F_{SO2}$), and molar ratios of H_2 to CO ($r = F_{H2}/F_{CO}$) on the activity of the catalyst (Cat-S) were investigated in order to determine the optimum operating conditions.

Tables 1 and 2 summarize the results of temperature dependence studies at a space velocity of $10,000\ h^{-1}$ and $15,000\ h^{-1}$, respectively. The experiments were carried out at r=3, and R=2. The results show that the conversion of SO_2 is >95% when the temperature is >380 C at both space velocities. Over the temperature range (340 C - 480 C) studied, the yield of H₂S does not show any appreciable and systematic changes: between 0.716 % and 3.31 % at a S.V.=10,000 h^-1, and between 0.919 % and 4.96 % at a S.V.=15,000 h^-1. However, the yield of COS shows a decrease with an increase of temperatures: Y_{COS} =2.75 % and 0.749 % at 340 C and 480 C, respectively (at a S.V.=10,000 h^-1); Y_{COS} =10.5 % and 0.178 % at 340 C and 480 C, respectively (at a S.V.=15,000 h^-1). AT a S.V.=10,000 h^-1, the yield of elemental sulfur, Y_{S2} is 93.7 % at 380 C and reaches a maximum value of 95.1 % at 420 C; it decreases slightly to 94.4 % with further increase of the temperature to 480 C. At a S.V.=15,000 h^-1, Y_{S2} is 92.8 % at 380 C, and reaches 94.9 % at 420 C.

The effect of space velocity on the catalyst was shown in Table 3. The conversion of SO_2 remains fairly stable (95.8 % - 98.7 %) in a S.V. range of 5,000 to 15,000 h⁻¹. At a S.V. =15,000 h⁻¹, it was observed that the temperature of the catalyst increased 60 degree C, which could be attributed to the liberation of heat from the reactions (exothermic reactions). Y_{HZS} remains at very low level (0.269 % - 0.716 %) when the S.V. is less than 10,000 h⁻¹, it shows a slight increase to 2.21 % as the S.V is increased to 13,750 h⁻¹, but it reaches 4.96 % as the S.V. is further increased to 15,000 h⁻¹. Y_{COS} remains very small (0.095 % - 1.32 %), and does not appeared to be affected systematically by the change of the space velocity. Y_{SZ} remains very high value (95.1 % -97.5 %) for S.V. up to 13,750 h⁻¹, it decreases to 92.3 % when the S.V. is increased to 15,000 h⁻¹.

Lifetime tests

The lifetime test was carried out continuously for $1080\,h$ (45 days). The flow rate of H_2 , CO, and SO₂ were 2286, 3047, and 2667 ml/h respectively. These correspond to R=2 and r=0.75. The amount of catalyst used was 1 g. These correspond to a space velocity of $10,000\,h^{-1}$. The catalytic activity was evaluated at three temperatures: 440, 460, and 480 C. The arithematic mean of the experimental results of all 45 days is shown in Table 4. Also given in Table 10 is the arithematic mean of results of an additional experimental condition which was implemented after 15 days lifetime test, and used r=3 to cover the composition of synthesis gas produced from methane.

The results indicate that the activity of the Cat-S, including the conversion and the selectivity, is very stable and does not show any changes during the entire 1080 h of the lifetime test. Table 10 shows that the yield of elemental sulfur ranges between 93.1 and 96.5%, which is far superior to results so far reported in the literatures [2,3,4]. These high yields were achieved at a space velocity of $10,000 \, h^{-1}$, compared with a reported result of obtaining 69.3 - 72.8% yield of elemental sulfur at a space velocity of $2,000 \, h^{-1}$, and a 82.8% sulfur yield at a space velocity of only $500 \, h^{-1}$. Table 10 shows that the yield of H_2S ranges between 1.28 and 2.82%, which is far better than those of other catalysts: 13.4% for NiO/Al₂O₃ [2] at a space velocity of $2000 \, h^{-1}$ and at $400 \, C$; 3.80% for Co_3O_3/Al_2O_3 [3] at a space velocity of $2000 \, h^{-1}$ and at $300 \, C$; 13.9% for NiO + Co_3O_4 [4] at a space velocity of $2000 \, h^{-1}$ and at $450 \, C$. The yield of H_2S increases along with the increase of the reaction temperatures. Therefore, it is remarkable to observe the low yield of H_2S for the Cat-S at a temperature of $440 \, to$ $480 \, C$.

Granules (d. 3 mm x h. 5 mm)

Parametric Studies

The effect of temperature, space velocity, and molar ratio of reactants on the activity and selectivity of the Cat-S catalyst on granules was studied. Table 5 and 6 show the effect of temperature on the catalyst at r=0.4 and 3 respectively. The results indicate that at a given temperature, C, Ys2, and Ss2 increase, while YH2S and YCOS decrease along with the increase of r. Meanwhile, C, YH2S, and Ss2 show an increase, while YCOS decreases, as the reaction temperature is increased at a given r value. At a space velocity of $2100 \, h^{-1}$ and R=2 (i.e. a stoichiometric ratio), the yield of sulfur increases to more than 90% when the temperature is above 560 C, 520 C, and 460 C with r=0.4, 0.75, and 3 respectively. It is worthy noting that the yield of sulfur reaches 97.8% at 560 C and a space velocity of 2100 h^{-1} with synthesis gas derived from methane (i.e. r=3).

The effect of the space velocity on the catalyst for r=3 was shown in Table 7 (480 C). The temperature of this series of experiments were chosen such that Y_{S2} could achieve more than 90%. The results indicate that C, Y_{H2S} , and Y_{S2} decrease, while Y_{COS} increases along with the increase of the space velocity. S_{S2} remains fairly constant under the experimental conditions employed.

The effect of R on the Cat-S at r=3 was summarized in Table 8 (480 C). The results show that at a given r value, C, Y_{H2S} , and Y_{COS} show a slight increase along with the increase of R until R reaches 2. Beyond that however, Y_{H2S} exhibits a drastic growth with the increase of R; Y_{COS} also shows some growth with R, but to a much lesser extent than Y_{H2S} . It is obvious that Y_{S2} is the greatest when R is 2 regardless of the ratio of r.

High Efficiency Recovery

Because of the incomplete conversion of SO₂, and the production of unwanted byproducts, H₂S and COS, either a tail gas treatment step or recycling the byproducts for combustion is necessary. Many technologies have been developed for the treatment of tail gas from a Claus process. However, the tail gas treatment cost is substantial. The combustion treatment would increase the concentration of SO₂ in flue gas. Therefore, it is desirable to maximize the yield of elemental sulfur and to minimize the production of byproducts.

The operating conditions of the Cat-S to obtain a Y_{S2} of 97 % have been determined. Table 9 and 10 show the effect of space velocity and temperature on the catalytic reduction of SO_2 by synthesis gas derived from methane to achieve a more than 93% Y_{S2} . Y_{S2} reaches between 96.9% and 97.1% at 520 C and a space velocity from 1,800 h⁻¹ to 2,000 h⁻¹; further increase of space velocity to 3,000 h⁻¹, Y_{S2} decreases to 93%. To achieve a Y_{S2} of 96% at a space velocity of 3,000 h⁻¹, the temperature of the catalytic reactions would have to be increased to 580 C (Table 28).

An alternative technology for the conversion of SO_2 to elemental sulfur involves two steps: 1. the combustion of SO_2 in a hydrocarbon flame under reduced conditions to form H_2S , 2. the employment of a Claus process to react SO_2 with H_2S to produce elemental sulfur. The first step requires the consumption of an excess amount of hydrocarbon, compared with the need of only a stoichiometric amount of synthesis gas for SO_2 reduction in the present invention. The Claus process requires three stages to achieve a 96-97% Y_{S2} at a space velocity of $1,500\text{-}3,000\text{ h}^{-1}$, while the new technology needs only a single stage reactor to obtain the same Y_{S2} at a comparable space velocity, $2,000\text{-}3,000\text{ h}^{-1}$.

CONCLUSION

We have developed a catalyst for reduction of SO₂ by synthesis gas. This catalyst is composed of a mixture of common transition metal oxides supported on —alumina and is inexpensive.

The inventive catalyst can achieve a high conversion efficiency of SO₂ by synthesis gas with a high selectivity to elemental sulfur. Unlike the Claus process, the reaction of SO₂ with synthesis gas to form elemental sulfur is not a reversible process. As a result, a high efficiency recovery of sulfur can be achieved in a single stage reactor.

A lifetime (1080 h) test has been successfully performed on the Cat-S in 30-40 mesh particle sizes. The test was conducted at 480 C, S.V. = $10,000 \, h^{-1}$, R = 2, and at r = 3 and 0.75. The activity of the catalyst remains very stable during the entire period of the lifetime test. The yield of sulfur was 96.5% and 94.1% at r = 3 and 0.75 respectively.

The mass balance of sulfur and carbon has been checked satisfactory by measuring the aforementioned products.

It has been demonstrated that the byproducts, H₂S and COS, produced during the conversion of SO₂ to sulfur can be circulated back to the feed gas for subsequent conversion on inventive catalysts without resulting in further accumulation of the said byproducts.

This catalyst can achieve 97% yield of elemental sulfur at 540 C with a space velocity of 2,000 h⁻¹ or at 640 C with a space velocity of 3,000 h⁻¹. This catalyst requires only a stoichiometric amount of synthesis gas for SO₂ reduction. While the waste of fuel is negligible, the operating cost is small

The inventive catalyst possesses very promising properties. As such, it could be utilized as a basis to develop a new process for high efficiency conversion of SO₂ to elemental sulfur by synthesis gas at a more cost effective manner than technologies available currently.

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ACKNOWLEDGEMENT

The authors appreciate the support of Perry Bergman, Charles Schmidt, and Charles Drummond. This work was supported by the Assistant Secretary for Fossil Energy, U.S. Department of Energy, under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

Table 1 The effect of temperatures on the Cat-S(particles) at (H2/CO)=3.0, and S.V.=10,000 h-1

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(15	YH2S	¹ cos	Y _{S2}	S _{S2}	- 1
(°C)	(%)	(%)	(%)	(%)	(%)	
340	83.7	1.59	2.75	79.4	94.8	
380	95.9	1.66	0.548	93.7	97.7	- 1
400	97.9	3.31	0.325	94.2	96.3	- 1
420	98.0	2.51	0.314	95.1	97.0	- 1
440	97.2	2.19	0.341	94.7	97.4	
460	96.3	1.57	0.326	94.4	98.0	- t
480	95.8	0.716	0.749	94.4	98.5	

Table 2 The effect of the temperatures on the Cat-S (particles) at (H2/CO)=3.0, and S.V.=15,000 h⁻¹

(°C)	C (%)	YH2S (%)	Y _{cos} (%)	Y _{S2} (%)	SS2 (%)
340	62.7	0.919	10.5	51.4	81.8
360	74.2	0.218	5.23	68.8	92.7
380	94.8	1.53	0.526	92.8	97.8
400	96.5	1.62	0.489	94.4	97.8
420	97.7	2.45	0.324	94.9	97.2
440	96.9	2.07	0.351	94.5	97.5
460	96.3	1.83	0.363	94.1	97.7
480	97.4	4.96	0.178	92.3	94.7

Table 3 The effect of the space velocity on the Cat-S (particles) at (H2/CO)=3.0, and 480 C

S.V. (h-1)	C (%)	YH2S (%)	Y _{cos}	YS2 .(%)	SS2 (%)
5000	97.7	0.289	0.095	97.4	99.0
6250	98.2	0.482	0.123	97.5	99.4
7500	97.9	0.349	0.839	96.7	98.8
8750	98.4	0.574	0.102	97.7	99.3
10000	95.8	0.716	0.746	94.4	98.5
11250	96.6	0.269	0.077	96.2	99.6
12500	98.7	2.29	1.32	95.1	96.3
13750	98.5	2.21	0.248	96.0	97.5
15000	97.4	4.96	0.178	92.3	94.7

Table 4 The arithmatic mean values of the lifetime test results at 440 C, 460 C, and 480 C; and at the feed gas molar ratio (H2/CO)=0.75 [* feed gas molar ratio (H2/CO)=3]

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t (*C)	C	YH2S	Ycos	Y _{S2}	S _{S2}		
(°C)	(%)	(%)	(%)	(%)	(%)		
440 460	95.7 96.2	2.30	0.356	93.1	97.0		
480	97.3	2.36 2.82	0.376	93.5	97.2 96.7		
480*	98.2*	1.28*	0.366 0.382*	94.1 96.5*	98.3*		
1400	1 70.2	1.20	0.302	יכיספן	1 30.0.		

Table 5 The effect of the temperatures on the Cat-S (granules) at (H2/CO)=0.4, [(H2+CO)/SO2]=2.0, and S.V.=2,105 h⁻¹

t	C	YH2S	Ycos	Y _{S2}	S _{S2}	
(°C)	(%)	(%)	(%)	(%)	(%)	
440	81.4	0.949	9.0	71.9	87.1	
460	85.7	0.992	6.09	78.6	91.7	
480	88.2	1.08	4.95	82.1	93.1	
500	91.7	1.37	3.56	86.8	94.6	
520	93.0	1.40	2.93	88.7	95.3	
540	93.5	1.42	2.42	89.7	95.9	
560	94.3	1.53	2.22	90.5	96.1	
580	96.7	2.47	2.17	92.0	95.3	

Table 6 The effect of the temperatures on the Cat-S (granules) at (H2/CO)=3.0, [(H2+CO)/SO2]=2.0, and $S.V.=2.105\ h^{-1}$

	(%)	YH2S (%)	Y _{cos} (%)	YS2 (%)	SS2 (%)	
440	91.4	0.414	2.80	88.2	96.5	
460	93.0	0.423	2.29	90.3	97.1	
480	94.4	0.442	1.88	92.1	97.5	
500	97.0	0.438	1.37	95.5	98.1	
520	97.7	0.516	1.13	96.1	98.3	
540	98.5	0.524	1.00	96.9	98.3	
560	99.3	0.740	0.782	97.8	98.4	
580	99.4	0.811	0.748	97.8	98.4	

Table 7 The effect of the space velocity on the Cat-S (granules) at (H2/CO)=3.0, [(H2+CO)]/SO2]=2.0, and 480 C

S.V. (h ⁻¹)	C (%)	YH2S (%)	Y _{cos} (%)	YS2 (%)	\$S2 (%)
1000	98.6	2.35	0.789	95.5	96.8
1500	97.3	0.791	1.05	95.5	98.1
1800	96.0	0.696	1.52	93.8	97.7
2000	94.4	0.442	1.88	92.1	97.5
2500	90.6	0.619	1.96	88.0	97.2
3000	86.5	0.623	2.26	83.7	96.7

Table 8 The effect of the molar ratio of reactants on the Cat-S (granules) at (H2/CO)=3.0, [(H2+CO)]/SO2]=2.0, S.V.=2.000 h⁻¹, and 480 C

	((111/CO/)/ SCE)-2:0, S.V2,000 II , and 400 C							
CO + H ₂ SO ₂	(%)	YH2S (%)	Y _{cos}	YS2 (%)	SS2 (%)			
3.0	99.8	35.1	1.59	63.2	63.3			
2.5	99.7	21.0	1.64	77.0	77.3			
2.2	99.8	6.61	1.72	91.4	91.7			
2.0	94.4	0.442	1.88	92.1	97.5			
1.8	92.9	0.339	1.64	91.0	97.9			
1.6	88.9	0.293	1.66	87.6	97.8			
1.4	84.1	0.302	1.63	82.8	97.7			

Table 9 The effect of the space velocity on the Cat-S (granules) at (H2/CO)=3.0, [(H2+CO)]/SO2]=2.0, and 520 C

S.V. (h ⁻¹)	(%)	YH2S (%)	Y _{cos} (%)	YS2 (%)	\$S2 (%)
1000	98.5	0.990	0.467	97.0	98.5
1500	98.2	0.445	0.772	96.9	98.8
1800 2000	98.9 98.5	1.05 0.624	0.791 1.00	97.1 96.9	98.1 98.3
2500	97.3	0.342	1.24	95.7	98.4
3000	94.8	0.337	1.47	93.0	98.1

Table 10 The effect of the temperatures on the Cat-S (granules) at (H2/CO)=3.0, [(H2+CO)/SO2]=2.0, and S.V.=3,158 h⁻¹

t (*C)	C (%)	YH2S (%)	Y _{cos} (%)	YS2 (%)	\$ _{\$2} (%)
540	95.3	0.479	1.30	93.5	98.1
560	96.1	0.536	1.06	94.5	98.3
580	97.6	0.614	1.00	96.0	98.3
600	98.3	0.979	0.882	96.5	98.1
620	98.4	0.920	0.755	96.8	98.3
640	98.6	0.931	0.621	97.0	98.4
660	98.8	1.36	0.441	97.0	98.2